STRUCTURAL, ELECTRONIC AND MAGNETIC PROPERTIES OF THE LINEAR CHAIN COMPOUNDS CsMI3(M = V, Cr, Mn) FROM 129I MÖSSBAUER SPECTROSCOPY

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Résumé.- L'analyse des spectres Mössbauer de ^{129}I dans les composés $CsMI_3$ (M = V, Cr, Mn) a permis de déduire la symétrie locale de l'ion de transition. Une étude complémentaire par diffraction de rayons X a montré que $CsCrI_3$ présente une transition de phase cristallographique à 165 K. Un ordre magnétique a été mis en évidence dans $CsCrI_3$ et $CsMnI_3$. Les densités de charge et de spin dans les orbitales de valence de l'iode ont été déduites à partir des paramètres d'interactions hyperfines. Un arrangement antiferromagnétique des moments le long de l'axe des chaînes est suggéré pour $CsMnI_3$.

Abstract.- The coordination symmetry of the M^{2+} ion in the compounds $CsMI_3$ (M = V, Cr, Mn) is deduced from ^{129}I Mössbauer spectroscopy. For $CsCrI_3$, a crystal phase transition is observed at 165 K. Magnetic transitions are observed for $CsCrI_3$ and $CsMnI_3$. The hyperfine interactions parameters are interpreted for the charge and spin densities in the iodine valence orbitals. An antiferromagnetic alignement of the spins along the chain axis is suggested for $CsMnI_3$.

The compounds $CsMI_3$ have attracted much interest in view of their linear chain structure which gives rise to predominantly one dimensional electronic and magnetic properties.

From previous single crystal X-ray diffraction studies of $CsVI_3$ and $CsMnI_3$, it was concluded that the space group of these compounds is either $P6_3/mmc$ or $P6_3mc$ /1/. However, for $CsMnI_3$, a more recent work has showed that the centrosymmetric $P6_3/mmc$ space group gave the best agreement with the measured intensities /2/. For both structures, the transition metal ion is surrounded by a distorded octahedron of halide ions. However, the M-I-M bridges are symmetric for the space group $P6_3/mmc$ whereas they are asymmetric for the lower symmetry $P6_3mc$ space group (figure 1). The ^{129}I Mössbauer measurements on powder samples reveal for both $CsVI_3$ and $CsMnI_3$ a single crystallographic iodine site with a positive quadrupole coupling constant (figure 2). These results allow to conclude that both compounds crystallize in the space group $P6_3/mmc$.

The ^{129}I Mössbauer spectra of $CsCrI_3$ measured below 100 K reveal the existence of two non-equivalent crystallographic iodine sites with relative occupation 1 : 2 (figure 2). The 27.8 keV Mössbauer resonance cannot be measured at higher temperatures because of the sharp decrease of the Debye-Waller factor. The occurence of two iodine sites is incompatible with either structure proposed from X-ray diffraction study performed at 300 K /1/.

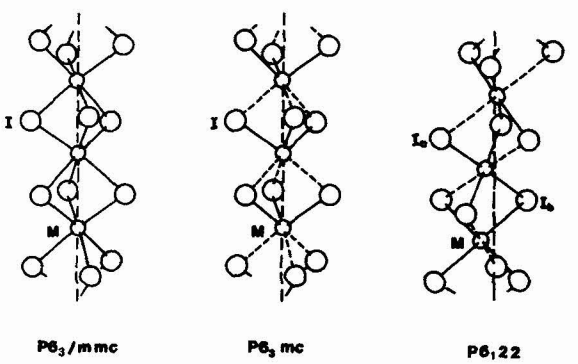

Fig.1 : Partial view of the linear chain showing the coordination symmetry of the transition metal ion for various space group.

Indeed, our investigation of the powder X-ray diffraction of $CsCrI_3$ as a function of temperature reveals a crystal phase transition at 165 $\pm$ 5 K from a high temperature hexagonal phase (a = 8.12 Å c = 6.85 Å) to a low temperature phase of lower symmetry (likely orthorhombic). In the low temperature phase the coordination of the Cr^{2+} ion is deduced from the Mössbauer results to be an axially distorted octahedron (figure 1), similar for instance to that of Cu in $CsCuCl_3$ which crystallizes in the $P6_122$ space group. A static Jahn-Teller

distortion may explain the crystal phase transition.

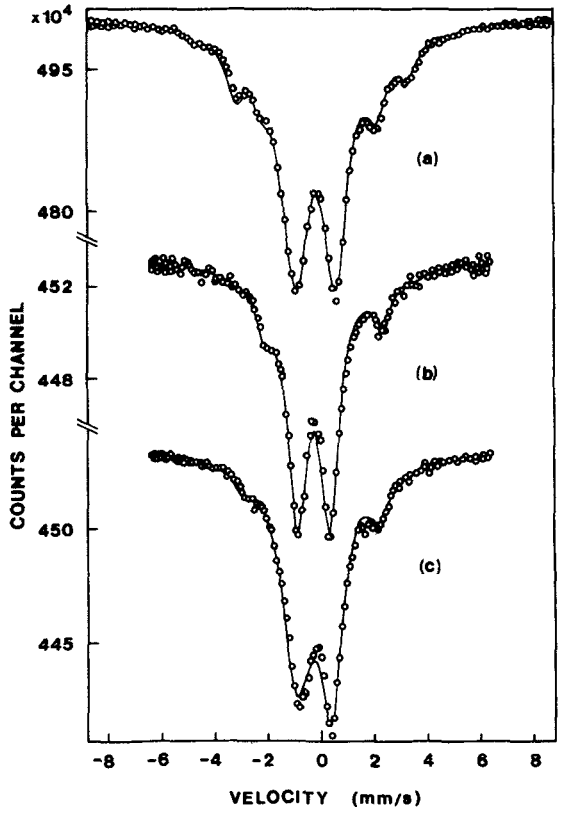

Fig. 2 : Mössbauer spectra of ^{129}I in $CsMI_3$.
a) $CsCrI_3$ at 77 K
b) $CsMnI_3$ at 21 K
c) $CsMnI_3$ at 1.4 K

Magnetic ordering is observed in $CsCrI_3$ and $CsMnI_3$; the 3d-order temperatures are 18 and 10 K respectively. Due to the poor spectral resolution connected with the low symmetry of the Cr^{2+} ion, the analysis of the magnetic data in $CsCrI_3$ is uncertain. In $CsMnI_3$, the interpretation of the transferred hyperfine field at the ^{129}I nucleus indicates an antiferromagnetic spin arrangement within the chains, with the magnetic moments of the Mn^{2+} ions directed parallel to the chain axis.

The charge densities in the valence orbitals of iodine are obtained from the analysis of the isomer shift and quadrupole interaction parameters. The spin densities are evaluated from the transferred magnetic hyperfine interaction /3/. Quantitative estimates for the bonding coefficients and details of the electronic and magnetic exchange mechanisms are drawn from these data (Table I).

Table I

Compound		N_s	N_{pz}	N_{px}	N_{py}	$f_\sigma - f_\pi$
$CsVI_3$		1.99	2*	1.84	1.90	-
$CsCrI_3$	a - site	1.99	1.81	1.93	2*	-
	b - site	1.99	2*	1.80	1.84	-
$CsMnI_3$		2	2*	1.84	1.90	1.5×10^{-2}

*assumed value.

Charge and spin densities at ^{129}I in $CsMI_3$ (M = V, Cr, Mn). N_s and N_{pi} represent the charge densities in the 5s and 5pi valence orbitals of iodine. f_σ and f_π are the spin densities in the $5p_\sigma$ and $5p_\pi$ orbitals respectively.

References

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